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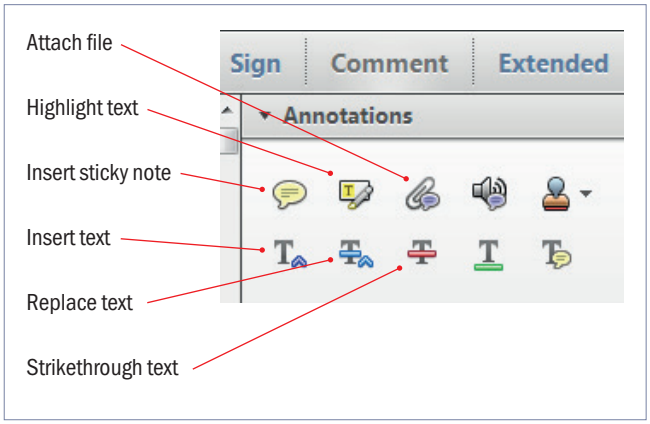

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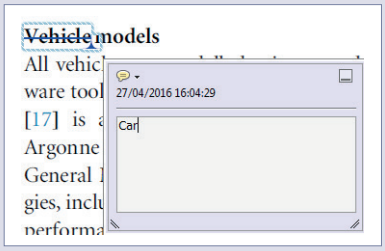

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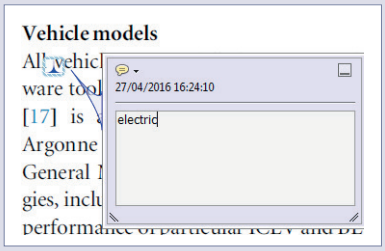

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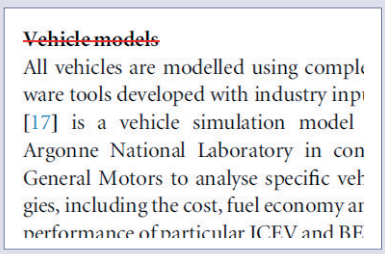

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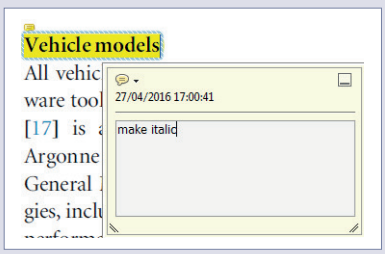

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Surface Topography: Metrology and Properties

PAPER

Comparative surface and adhesion properties of mechanical abrasion, flame and radiation-based surface treated wood plastic composites made with different polymers

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Abstract

Wood plastic composites (WPCs) show low surface energy and poor adhesion properties, and they can be improved by applying surface treatment. In this study three WPCs made with polyethylene, polypropylene and poly(vinyl chloride) have been treated by mechanical abrasion, flame and radiation-based (UV/ozone, atmospheric pressure plasma torch, Ar:O_2 low pressure plasma) treatments. The influence of the wood content and polymer nature in the WPC on the surface modifications and adhesion properties produced by the surface treatments has been assessed. The surface treatments by mechanical abrasion and flame produced slight changes in the WPC surface, mainly in roughness, irrespective of the wood content and polymer nature in the WPC. The radiation-based surface treatments were the most efficient in increasing the surface energy (particularly the polar component) and produced ablation and surface oxidation of the WPC, the most noticeable modifications were obtained in the WPCs made with polyolefin. The adhesion (180° peel strength and cross-hatch adhesion) of the WPCs made with polyolefin was enhanced by surface treatment with both plasmas, irrespective of the adhesive or coating nature, and a relationship between the surface modifications produced by the plasma treatments and the adhesion was found. The surface modifications by the different treatments were less marked for the WPC made with poly(vinyl chloride) due to its smooth surface, low wood content and the existence of carbonate filler in its composition; furthermore, lower adhesion than for the surface treated WPCs made with polyolefin was obtained, and the highest 180° peel strength and cross-hatch adhesion were obtained with different surface treatments, the adhesion also depended on the coating nature. The effectiveness of the surface treatment in improving the adhesion of the WPCs depended on their wood content, polymer nature and surface roughness.

1. Introduction

Wood plastic composites (WPCs) are materials widely employed as outdoor furniture and decking, and in building industry. WPCs appearance is somewhat similar to that of wood having better mechanical properties, lower biodegradability and higher durability; these properties are imparted by the polymer in the composite formulation which, during processing, is accumulated on the outermost surface. The general composition of the WPCs consists in 30–70 wt% polymer—polyethylene (PE), polypropylene (PP) and poly (vinyl chloride) (PVC) are the most commonly used, 30–70 wt% wood flower, and small amounts of additives (compatibilisers, processing aids, fillers). Because of the WPC surface is enriched in polymer, its surface properties are quite similar to the ones of the polymers in its composition. Polyolefins have low surface energy and PVC contains plasticizers, and therefore the WPC surface shows low polarity and poor adhesion properties [1–3]. Although the pieces of WPC can be joined by mechanical interlocking or nails, these procedures are limited in irregular shaped pieces. Furthermore, the color of the WPC is generally imparted by adding colorants or dyes during manufacturing and they are difficult to paint [4].

Therefore, the possibility of joining the pieces of WPC with adhesives or coating them by means of paints or coatings is attractive. For good adhesion, the surface energy of the WPC must be higher than the one of the adhesive or coating which is usually higher than 40 mJ m^{-2}. Because of the low surface energy of the WPC, its adhesion is insufficient and an increase of the surface energy is required. The application of surface treatments allows the increase of the surface energy of the WPC [5, 6].

Several surface treatments have been proposed in the literature for improving the WPC surface properties, and the compared effectiveness of mechanical, chemical and flame surface treatments applied to different WPCs made with polyolefin have been studied elsewhere [5–9]. Gramlich *et al* [5] applied chemical and flame surface treatments (chromic acid, flame, water, flame+water) for improving the surface properties of WPC made with PP, and they concluded that the surface treatments with flame and chromic acid were the most effective because of the oxidation produced on the outermost PP surface. Oporto *et al* [7] used mechanical abrasion and heating of WPC surface for improving the adhesion of WPC to two-component epoxy adhesive, concluding that they were less effective than the flame treatment. Dimitrou *et al* [6] have employed the surface treatments with hydrogen peroxide and halogen lamps for WPCs but they produced poor adhesion. Moghadamzadeh *et al* [8] have proposed the surface treatment with flame, corona discharge, mechanical abrasion and a combination of mechanical abrasion and corona discharge for WPC made with high density polyethylene, and they found improved pull-off adhesion strength with all surface treatments, the highest adhesion was obtained for the combined surface treatment of mechanical abrasion and corona discharge. Gupta *et al* [9] have compared the effectiveness of the surface treatments with O_2 low pressure plasma and benzophenone/UV irradiation of WPCs made with PE and PP and improved adhesion was always obtained. Among the different surface treatments of WPCs described in the existing literature, the most effective was the surface treatment with chromic acid, but due to environmental concerns it has to be substituted. On the other hand, the surface treatment with O_2 low pressure plasma improved more than two-fold the peel strength, and, during the last few years, additional surface treatments for WPCs made with polyolefin have been proposed including UV/ozone, dielectric barrier discharge, and atmospheric pressure plasma torch, all them improved the surface properties and the adhesion of the WPCs [10–17]. However, a comparison of the effectiveness of these surface treatments in WPCs made with polymers different than PE and PP has not been carried out yet.

Although there are some publications dealing with the compared effectiveness of mechanical, chemical and flame surface treatments of WPCs made with polyolefin, the influence of the polymer nature and the wood content of the WPC have not been considered yet. Furthermore, the surface treatment of WPC made with PVC has been scarcely studied [12], and the most recent proposed radiation-based surface treatments for WPCs have not been compared. Therefore, in this study the surface modifications and adhesion of three WPCs made with PE, PP and PVC and different wood content treated with mechanical abrasion, flame and several radiation-based treatments (UV/ozone, atmospheric pressure plasma torch, Ar:O_2 low pressure plasma) to acrylic adhesive and coatings of different nature have been carried out.

2. Experimental

2.1. Materials

Three commercial WPCs made with different polymer matrices have been surface treated by mechanical abrasion, flame and radiation-based treatments:

- WPC made with PE (PE-WPC) was supplied by Condepols Company (Jaén, Spain) in alveolar boards obtained by extrusion. It contains 30 wt% high density polyethylene (HDPE) and 65 wt% wood component. The received alveolar board was cut into smaller pieces (3 × 7 cm^2) for carrying out the surface treatments.
- WPC made with PP (PP-WPC) was supplied by SCT-Straw (Barcelona, Spain) and was prepared by extrusion. It contains 70 wt% wood particles and 30 wt% PP. The received solid WPC profile was cut into smaller pieces (4 × 4 cm^2) for carrying out the surface treatments.
- WPC made with PVC (PVC-WPC) was supplied by Plásticos Víters S.A. (Valencia, Spain) as solid rectangular board. It contains 50 wt% of wood fibers, about 40 wt% PVC and non-disclosed additives. The received solid board was cut into smaller pieces (3 × 7 cm^2) for carrying out the surface treatments.

2.2. Surface treatments

2.2.1. *Treatment by mechanical abrasion*

Different sandpapers of P220 up to P400 grit sizes were placed on the upper round plate of 180 mm diameter of YA-20M sander (Yagüe Importaciones, Silla, Spain). The WPC piece was tightly held in the bottom base of the sander. The speed of the upper plate was varied between 180 and 2270 rpm and the abrasion time was set to 10 s. After abrasion of the WPC surface, the dust was removed with air pressurized gun. The optimal performance of the mechanical abrasion of the WPCs was obtained with P220 sandpaper grit and 1280 rpm.

2.2.2. *Flame treatment*

Flame treatment of the WPC surface was carried in Arcogas FTS 101 DR system (Arcogas GmbH, Mönsheim, Germany) by using mixtures of 33 l min^{-1} air and 1 l min^{-1} n-butane. WPC was placed

on air pressurized controlled platform for the flame treatment and the platform speed was varied between 0.1 and 1 m s^{-1}. The distance between the WPC surface and the flame torch was set to 1 cm. The optimal performance of the flame treatment corresponds to speed of the platform of 0.1 m s^{-1}.

2.2.3. UV/ozone treatment

UV/ozone surface treatment was carried out inside a box made of UV resistant polycarbonate provided with three low-pressure vapor grid mercury lamps (American Ultraviolet, Lebanon, IN, USA) with the main emission at wavelengths of 184.9 and 253.7 nm. The power of each UV lamp is 10 mW cm^{-2} measured at a distance of 2.54 cm between the UV lamp and the WPC surface. In order to avoid over-heating of the UV lamps, an exhaust fan was placed in one side of the polycarbonate box and the constant concentration of ozone during the treatment was maintained by a continuous entrance of fresh air throughout the opposite side of the polycarbonate box [17]. The time of UV/ozone exposure and the distance between the UV lamps and the WPC surface was varied. The time was varied between 1 and 10 min and the distance between the UV lamps and the WPC surface was varied between 1 and 5 cm. The optimal conditions of UV/ozone surface treatment were obtained for a distance of 1 cm and for 10 min of treatment.

2.2.4. Treatment with atmospheric pressure plasma torch

The surface treatment of the WPCs with atmospheric pressure plasma torch was carried out in FG1001 plasma generator (Plasma Treat GmbH, Steinhagen, Germany) provided with rotary nozzle RD1004 that has an opening ring of 4 mm diameter with rotational speed to 1900 rpm and an angle shot of 14°. The plasma was generated inside the nozzle by a non-equilibrium discharge using kHz excitation (voltage of 300 V and current of 8.6 A) and expelled through a circular orifice onto the WPC surface. The atmospheric pressure plasma was generated with compressed synthetic air (Air Liquide, Madrid, Spain), the pressure was set to 2.5 bars. The spelled plasma was directed to the surface of the WPC placed on movable platform which speed can be varied for changing the length of the treatment. The optimization of the atmospheric pressure plasma torch surface treatment of WPC was carried out in previous study [12], the best experimental conditions were a distance between the WPC surface and the nozzle of 1 cm and a platform speed of 1 m min^{-1}.

2.2.5. Treatment with Ar:O_2 low pressure plasma

Low pressure plasma reactor Digit Concept NT1 (BSET EQ, Antioch, CA, USA) was used and the plasma was generated by using a mixture of argon:oxygen (2:1, vol/vol; oxygen flow: 50 standard cm^3 min^{-1}; argon flow: 110 standard cm^3 min^{-1}). The shelves inside the plasma reactor were placed in direct working mode, the power was set to 200 W, and the residual pressure was set to 800 mbar. This surface treatment was optimized in a previous study [10], the best performance was obtained by using a length of treatment of 90 s.

Table 1. Optimal surface treatment conditions of the WPCs.

Surface treatment	Optimal conditions
Mechanical abrasion	Sandpaper P220; 1280 rpm
Flame	1 cm; 0.1 m s^{-1}
UV/ozone	1 cm; 10 min
Atmospheric pressure plasma torch	1 cm; 1 m min^{-1}
Ar:O_2 low pressure plasma	Direct; 200 W; 90 s

The optimal conditions for the surface treatments of the WPCs are summarized in table 1.

2.3. Experimental techniques

2.3.1. Attenuated total reflectance infrared spectroscopy (ATR-IR)

The chemical modifications of the WPCs produced by the different surface treatments were assessed by attenuated total reflectance infrared spectroscopy in Tensor 27 spectrometer (Bruker Optiks, Ettlingen, Germany) equipped with diamond prism. 60 scans were recorded with a resolution of 4 cm^{-1} and IR beam incidence angle of 45° was used. Under these experimental conditions, a depth of 10–15 μm of the WPC surface was analyzed.

2.3.2. Contact angle measurements and surface energy

The contact angle values at 25 °C of the as-received and surface-treated WPCs were measured in Ramé-Hart 100 goniometer (Netcong, NJ, USA). Two liquids of different polarities—bidistilled and deionized water (polar liquid) and diiodomethane (non-polar liquid)—were used. For measuring the contact angles, 4 μl drops of the test liquid were placed on the WPC surface and the contact angles were measured just after drop deposition on both sides of the drops. A minimum of five drops of each test liquid were placed on different places of the WPC surface and the values obtained were averaged.

By using the contact angle values obtained with water and diiodomethane, the surface energy (γ_s) and their polar (γ_S^p) and dispersive (γ_S^d) components of the as-received and surface treated WPCs was calculated by using Owens-Wendt approach—equation (1):

$$(1+\cos_i)\left(\gamma_i{}^d+\gamma_i{}^p\right)=2\left(\sqrt{\gamma_i{}^d\gamma_S{}^d}+\sqrt{\gamma_i{}^p\gamma_S{}^p}\right) \quad (1)$$

where θ_i is the contact angle, γ_i is the surface tension of the test liquid, and the superscripts *d* and *p* indicate the dispersive and polar components of the surface tension of the test liquid respectively. The surface tensions of the test liquids and their polar and dispersive components were $\gamma_{water}^p = 51$ mN m^{-1} and $\gamma_{water}^d = 21.8$ mN m^{-1}, and $\gamma_{CH_2I_2}^p = 0$ mN m^{-1} and $\gamma_{CH_2I_2}^d = 50.8$ mN m^{-1}.

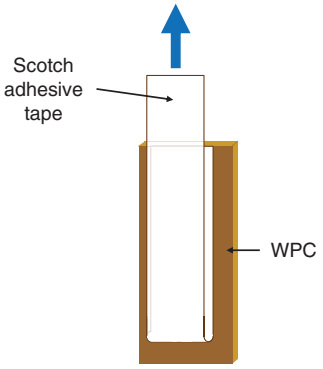

Figure 1. Scheme of 180° peel test.

2.3.3. Scanning electron microscopy (SEM)

The topographies of the as-received and surface treated WPCs were assessed by SEM in Jeol JSM-840 microscope (Jeol Ltd., Tokyo, Japan) working at an accelerating voltage of 15 kV. Prior to analysis, the WPCs were gold coated in Au/Pd metallizer Balzers SCD 004 (Oerlikon Surface Solutions, Balzers, Liechtenstein).

2.3.4. Adhesion measurements

The adhesion of the as-received and surface treated WPCs was assessed by using two different methods, 180° peel test of WPC/acrylic adhesive tape joints and cross-hatch of coated WPC.

180° peel tests of as-received and surface treated WPC/acrylic adhesive tape joints (figure 1) were carried out in TA-XT2i texture analyzer equipment (Stable Micro Systems, Godalming, UK), a pulling rate of 10 mm s^{-1} was used. Rectangular pieces of WPCs—dimensions of 3 × 7 cm^2 for PE-WPC and PVC-WPC, and 4 × 4 cm^2 for PP-WPC and rectangular pieces of Magic Scotch® tape (3M, Saint Paul, MN, USA) of 18 × 1.9 cm^2 were used. The adhesive tape was 11 cm longer than that of the WPC to facilitate the attachment to the upper clamp of the test machine for the 180° peel test (figure 1), and it was placed over the WPC surface covering the whole 7 cm length of the piece. Then, 2 kg rubber roller was passed 30 consecutive passes over the joint for achieving an intimate contact between the WPC surface and the acrylic adhesive tape. The long adhesive tape was attached to the upper clamp of the equipment, and the WPC piece was attached to the bottom clamp.

Cross-hatch adhesion test of WPC coated with two coatings of different nature was carried out according to ASTM D3359 standard. The test consists in the creation of 6 parallel cuts on the coated WPC by means of 0302001 blade device (Neurtek Instruments S.A., Eibar, Spain), applying a piece of standard Tesa® adhesive tape on the cuts, and after left the tape in contact with the cuts for 90 s, the tape was peeled at an angle near 180°. The cross-hatch adhesion was estimated by counting the number of detached squares of the coating and by assigning a code according the scale given in figure 2. Thus, a cross-hatch adhesion value of 5B means excellent adhesion as no coating squares are detached from the WPC surface; a cross-hatch adhesion value of 0B means poor adhesion because more than 65% of coating squares are detached.

For cross-hatch adhesion test, two commercial coatings of different nature were used, solvent-born modified silane polyurethane (PU)—Sintex MS-35 Plus (Quilosa-Selena Iberia, Madrid, Spain)—and waterborne polyvinyl acetate (PVA)—Caryal R-1 (Paniker S.L., Barcelona, Spain). Both coatings were applied by brush on the surface of the as-received and surface-treated WPC pieces, the thickness was controlled by means of 200 μm metering rod. The PU coating was let to cure at 25 °C during 4 weeks, and the PVA coating was cured at 25 °C during 24 h before testing. Two replicates of each coating were carried out and the results obtained were averaged.

3. Results and discussion

3.1. Surface characterization of the as-received WPCs

The WPCs have been characterized by TGA [17] for assessing their composition and the existence of inorganic additives. According to table 2, PE-WPC and PP-WPC show nearly the same thermal decomposition temperatures and weight losses, although PP-WPC has lower water content. However, PVC-WPC has lower wood content than the other WPCs and an additional thermal decomposition at 684 °C due to carbon dioxide appears, indicating the existence of carbonate filler in the formulation. The presence of carbonate filler is confirmed by the final inorganic solid residue of 16 wt% obtained in air atmosphere at the end of TGA experiment.

The ATR-IR spectra of the as-received WPCs are shown in figure 3. The ATR-IR spectra of PE-WPC and PP-WPC show similar C-H bands at 2840–2940 cm^{-1} (–CH stretching) and 1375–1455 cm^{-1} (–CH_2 bending). The ATR-IR spectrum of PVC-WPC shows the –CH stretching bands at 2840–2940 cm^{-1}, and the typical bands of PVC at 1420 cm^{-1} (–CH_2 bending) and 870 cm^{-1} (C-Cl band) appear. On the other hand, the bands corresponding to wood component at 3340–3350 (broad band due to –OH stretching), 1630–1640 (C-C stretching band), and 1023 cm^{-1} (intense band of C-O groups in cellulose) can be distinguished in the ATR-IR spectra of all WPCs (figure 3), their intensities vary depending on the amount of wood in the WPC. The highest intensities of the wood bands correspond to PE-WPC and the lowest to PVC-WPC.

Stark *et al* [18] proposed a method for determining semi-quantitatively the amount of wood component ('wood index') in WPCs by using the intensity of different bands of their IR spectra. In previous study [12], the wood index values of the WPCs were calculated as the ratio of the intensities of the IR bands at 1023 cm^{-1} (due to the wood) and at 2912 cm^{-1} (due to the

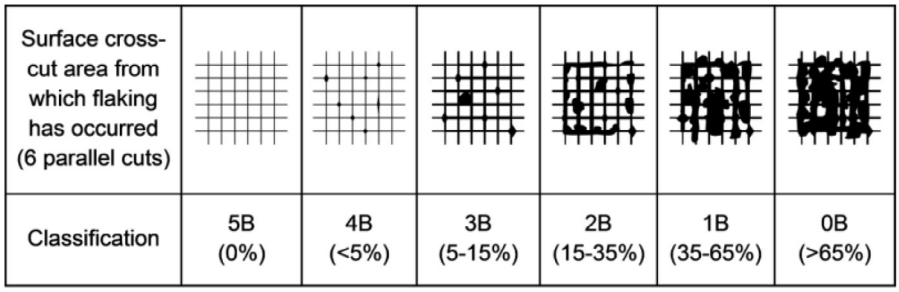

Figure 2. Cross-hatch adhesion scale according to ASTM D3359 standard [17].

Table 2. Main thermal decompositions of the as-received WPCs. TGA experiments [17].

	PE-WPC		PP-WPC		PVC-WPC	
Compound	T (°C)	Weight loss (%)	T (°C)	Weight loss (%)	T (°C)	Weight loss (%)
Water	70	4	159	4	31	1
Wood	291, 345	43	328	48	258, 279	28
Polymer	449	37	454	35	441	34
CO_2	–	–	–	–	684	6
Residue at 800 °C (N_2)	800	16	800	13	800	31
Residue at 800 °C (Air)	800	2	800	0	800	16

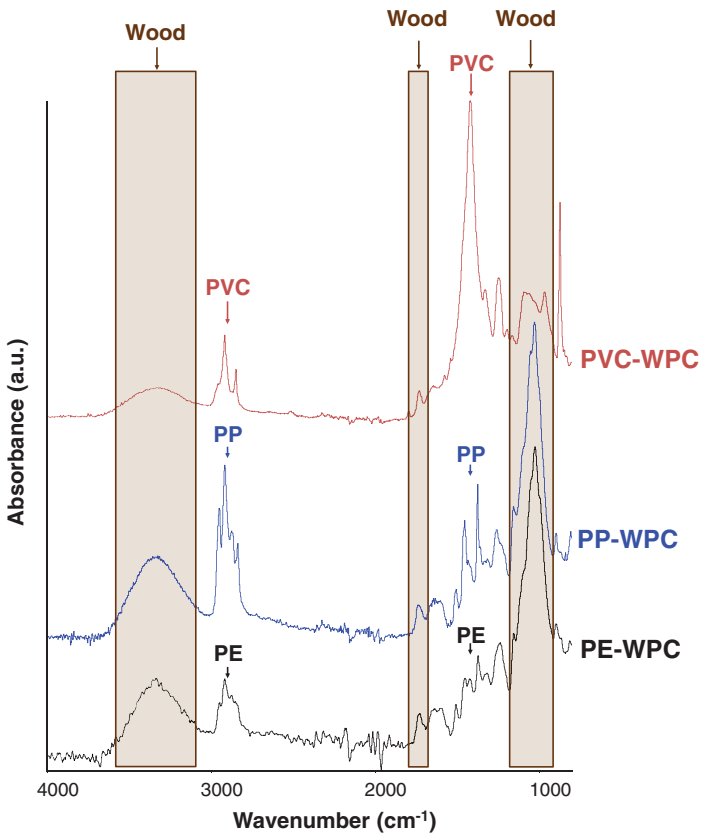

Figure 3. ATR-IR spectra of the as-received WPCs. Diamond prism.

polymer). The values of the wood indexes of the WPCs are given in table 3 and PE-WPC has the highest wood content and PVC-WPC has the lowest.

The wettability of the WPC surface was evaluated by contact angle measurements. According to table 4, the water contact angle values on PE-WPC and PP-WPC are higher than 100° indicating poor wettability, particularly in PP-WPC; however, the water contact angle of PVC-WPC is lower because of the higher polarity of the PVC polymer on the WPC sur-

Table 3. Wood index values of the WPCs [12].

WPC	Wood index (a.u.)
PE-WPC	332
PP-WPC	179
PVC-WPC	60

Table 4. Values of contact angles (25 °C) and surface energies and their polar and dispersive components for the as-received WPCs.

	Contact angle at 25 °C (degrees)		Surface energy (mJ m^{-2})		
WPC	H_2O	CH_2I_2	γ_s^p	γ_s^d	γ_s
PE-WPC	105	34	0	39	39
PP-WPC	111	65	0	26	26
PVC-WPC	83	65	7	21	28

face as compared to the ones of PE and PP; however, the diiodomethane contact angle value on PVC-WPC is higher than expected likely due to the higher content of polymer on the surface. The surface energies of the WPCs are given in table 4. All surface energies are low (except the one of PE-WPC) and they correspond to dispersive component; the existence of small polar component in PVC-WPC is consistent with the existence of carbonate filler on the surface. The lowest surface energies correspond to PP-WPC and PVC-WPC. The relatively high surface energy of PE-WPC can be ascribed to its higher wood content and/or the existence of roughness.

The surface roughness of the as-received WPCs was analyzed by SEM. Figure 4 shows the rough PE-WPC and PP-WPC surfaces and the relatively smooth PVC-WPC surface. The surface roughness is different in the WPCs and more important in PE-WPC than in PP-WPC; furthermore, all WPC surfaces are enriched in polymer, particularly PVC-WPC.

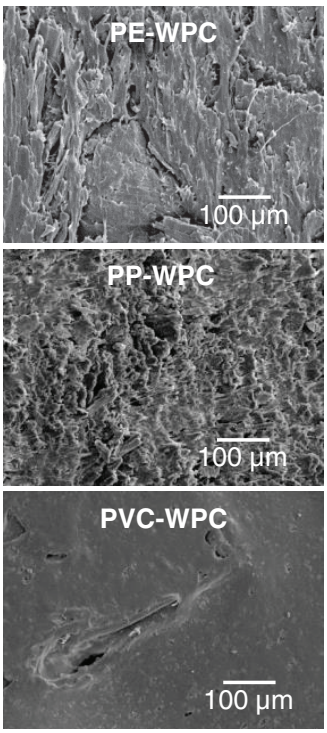

Figure 4. SEM micrographs of the as-received WPCs.

3.2. Characterization of the surface treated WPCs

The chemical modifications produced by surface treatment of the WPCs have been studied by ATR-IR spectroscopy. Figure 5(a) shows the ATR-IR spectra of the as-received and surface treated PE-WPC. The ATR-IR spectrum of PE-WPC treated by mechanical abrasion is similar to the one of the as-received composite and the ATR-IR spectrum of the flame treated PE-WPC shows less intense C-H stretching bands at 2840–2940 cm^{-1}, indicating the removal of polyethylene from the surface. The most important chemical changes of the PE-WPC surface are observed when it is treated with radiation-based surface treatments, i.e. UV/ozone, atmospheric pressure plasma torch and low pressure plasma. All these treatments increase the intensity of the bands due to polyethylene (2840–2950 cm^{-1}, 1373–1453 cm^{-1}) and the intensities of the bands due to wood are reduced, particularly in the atmospheric pressure plasma torch and UV/ozone treated PE-WPC. Furthermore, all radiation-based treatments produce some surface oxidation (increase of the C=O stretching band at 1730 cm^{-1}).

Figure 5(b) shows the ATR-IR spectra of the as-received and surface treated PP-WPC. The ATR-IR spectra of the PP-WPC treated by mechanical abrasion, flame and UV/ozone are similar, and they show a decrease in the intensity of the bands due to polypropylene, because of the removal of the polymer from the surface. Similarly, the ATR-IR spectrum of the low pressure plasma treated PP-WPC shows a moderate removal of polypropylene from the surface and oxidation is not noticed, anticipating the dominant effect of abrasion over chemical modification. The treatment with atmospheric pressure plasma torch is the only one able to produce an important removal of wood from the surface and the oxidation of the polypropylene (evidenced by the increase in the intensities of the C=O bands at 1630 and 1730 cm^{-1}—figure 5(b)) is also noticed. Therefore, the changes in the chemistry of the PP-WPC surface produced by the different treatments of are much less marked than for PE-WPC.

Figure 5(c) shows the ATR-IR spectra of the as-received and surface treated PVC-WPC. The mechanical abrasion and flame surface treatments decrease the intensity of the –OH band at 3300 cm^{-1} due wood and, for the flame treatment only, an increase of the intensities of the bands due to poly(vinyl chloride) is produced. The UV/ozone treatment of PVC-WPC increases the intensity of the –OH band due to wood and produces some surface oxidation—evidenced by the increase in the intensities of the C=O bands at 1730 and 1630 cm^{-1}. The surface treatment with

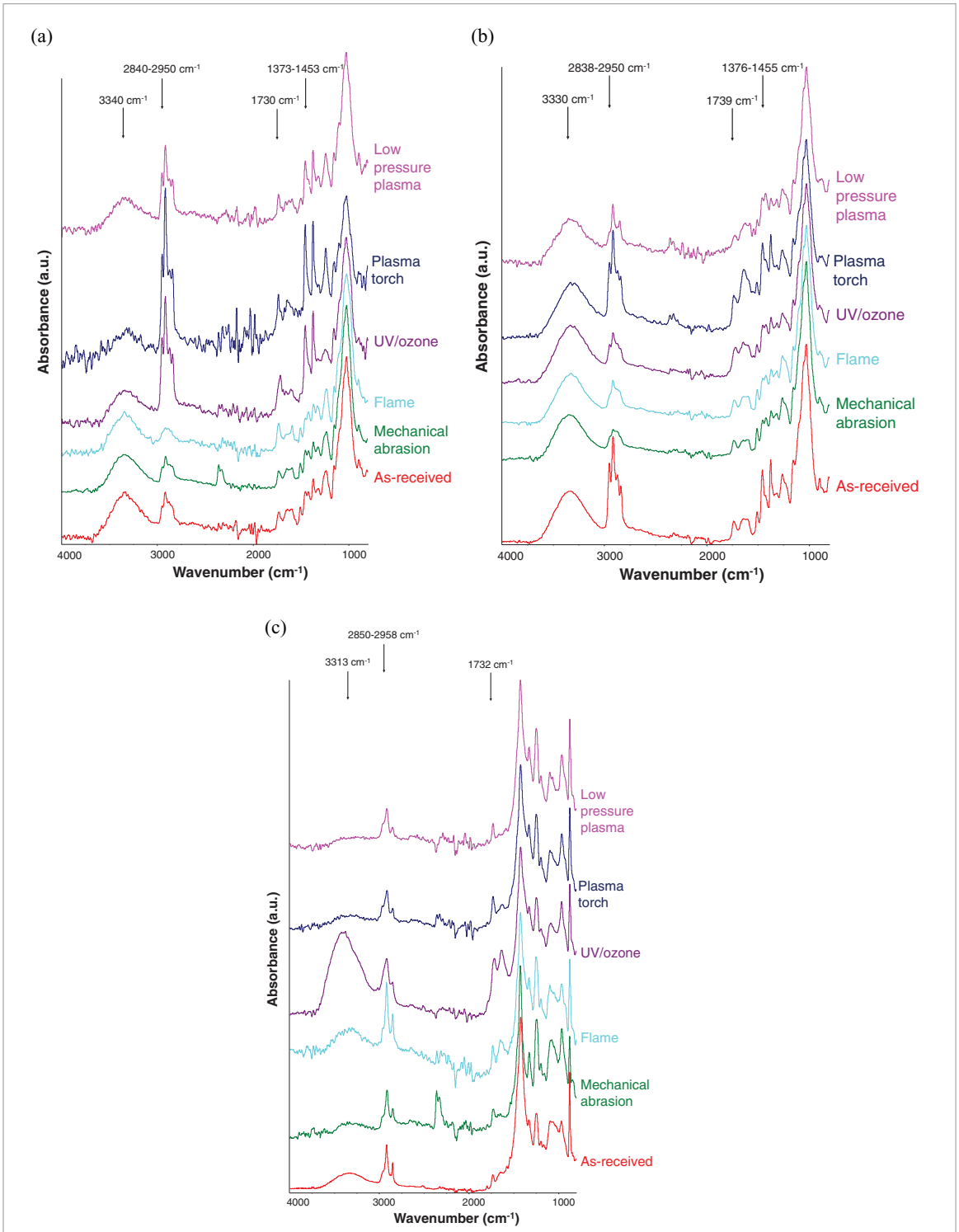

Figure 5. (a) ATR-IR spectra of the as-received and surface treated PE-WPC. Diamond prism. (b) ATR-IR spectra of the as-received and surface treated PP-WPC. Diamond prism. (c) ATR-IR spectra of the as-received and surface treated PVC-WPC. Diamond prism.

both plasmas produces the most important chemical changes in PVC-WPC and they consist in the increase of the intensity of the CH stretching bands at 2840–2940 cm^{-1} and CH bending bands of 1370–1450 cm^{-1} of the poly(vinyl chloride), and the surface oxidation is evidenced by the increase in the intensities of the C=O bands at 1730 and 1630 cm^{-1}. Therefore, due to its lower wood content and the existence of carbonate filler, the surface treatment of PVC-WPC produces more noticeable exposure of polymer to the surface than in the surface treated PE-WPC and PP-WPC, and therefore, more noticeable oxidation is produced.

The chemical changes produced by the different surface treatments should modify the wettability and surface energy of the WPCs. Figure 6(a) shows the surface energies and their dispersive and polar components of the as-received and surface treated PE-WPC. All surface treatments increase the surface energy of PE-WPC, particularly the UV/ozone, atmospheric pressure plasma torch and low-pressure plasma

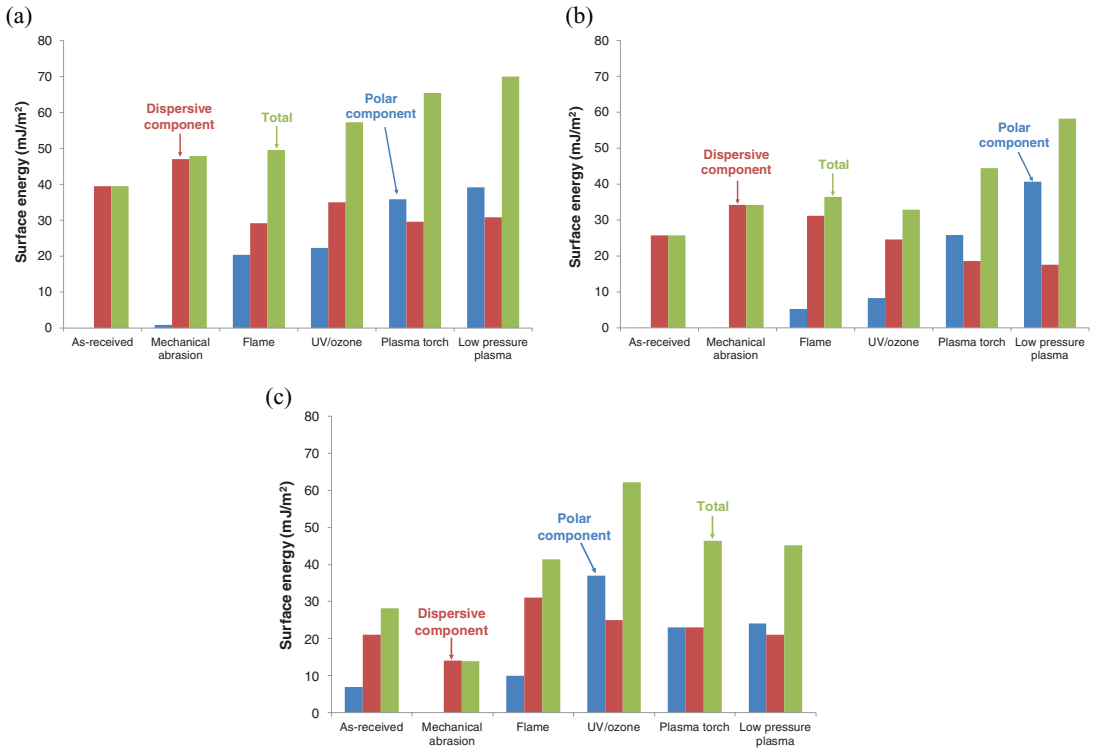

Figure 6. (a) Surface energies and their polar and dispersive components for the as-received and surface treated PE-WPC. (b) Surface energies and their polar and dispersive components for the as-received and surface treated PP-WPC. (c) Surface energies and their polar and dispersive components for the as-received and surface treated PVC-WPC.

treatments. The mechanical abrasion increases moderately the surface energy of PE-WPC and it is mainly due to an increase in the dispersive component, this can be ascribed to changes in the surface roughness (figure 7(a)). The UV/ozone and flame surface treatments increase the surface energy of PE-WPC to 50–60 mJ m^{-2} and this increase is due to an important decrease of the dispersive component and a noticeable increase of the polar component (above 20 mJ m^{-2}) of the surface energy. The increase in the polar component of the surface energy of PE-WPC indicates that the UV/ozone and flame treatments produce surface oxidation and/or changes in the surface roughness.

The surface energies and their dispersive and polar components of the as-received and surface treated PP-WPC are given in figure 6(b). Similar to the surface treated PE-WPC, the mechanical abrasion treatment increases moderately the surface energy of PP-WPC and it is mainly due to an increase in the dispersive component, which is likely associated to the decrease of the surface roughness. The UV/ozone and flame surface treatments produce a similar moderate increase of the surface energy of PP-WPC than the mechanical abrasion does, but there is a slight decrease of the dispersive component and a slight increase of the polar component (lower than 10 mJ m^{-2}) of the surface energy. The variation of the surface energies of the UV/ozone and flame treated PP-WPC is in good agreement with the similarity in their ATR-IR spectra (figure 5(b)). Similar to PE-WPC, the highest increase in the surface energy (mainly due to the increase of the polar component) of PP-WPC is produced by treatment with low-pressure plasma; however, the maximum surface energy of the treated PP-WPC is lower than 60 mJ m^{-2}.

The surface energies and their dispersive and polar components of the as-received and surface treated PVC-WPC are given in figure 6(c). The mechanical abrasion treatment decreases noticeably the surface energy of PVC-WPC due to the creation of surface roughness (figure 7(c)) and to the removal of wood and carbonate filler as well. The flame surface treatment increases the surface energy of PVC-WPC to 41 mJ m^{-2} and this increase is due to important ablation (figure 7(c)), because of the increase is due only to the dispersive component of the surface energy. Both plasma treatments improve the surface energy of PVC-WPC up to 47 mJ m^{-2} because an important increase of the polar component is produced due to surface oxidation. The highest surface energy (higher than 60 mJ m^{-2}) of PVC-WPC is obtained by treatment with UV/ozone, because of the enrichment of the surface in wood component and the creation of new C=O groups, this justify the important contribution of the polar component. Therefore, the effects of the surface treatments are less marked in PVC-WPC than in the other WPCs.

The changes in the surface energies of the surface treated WPCs are also affected by changes in their topography. The SEM micrographs of the as-received and surface treated PE-WPC are given in figure 7(a). The SEM micrograph of the as-received PE-WPC shows

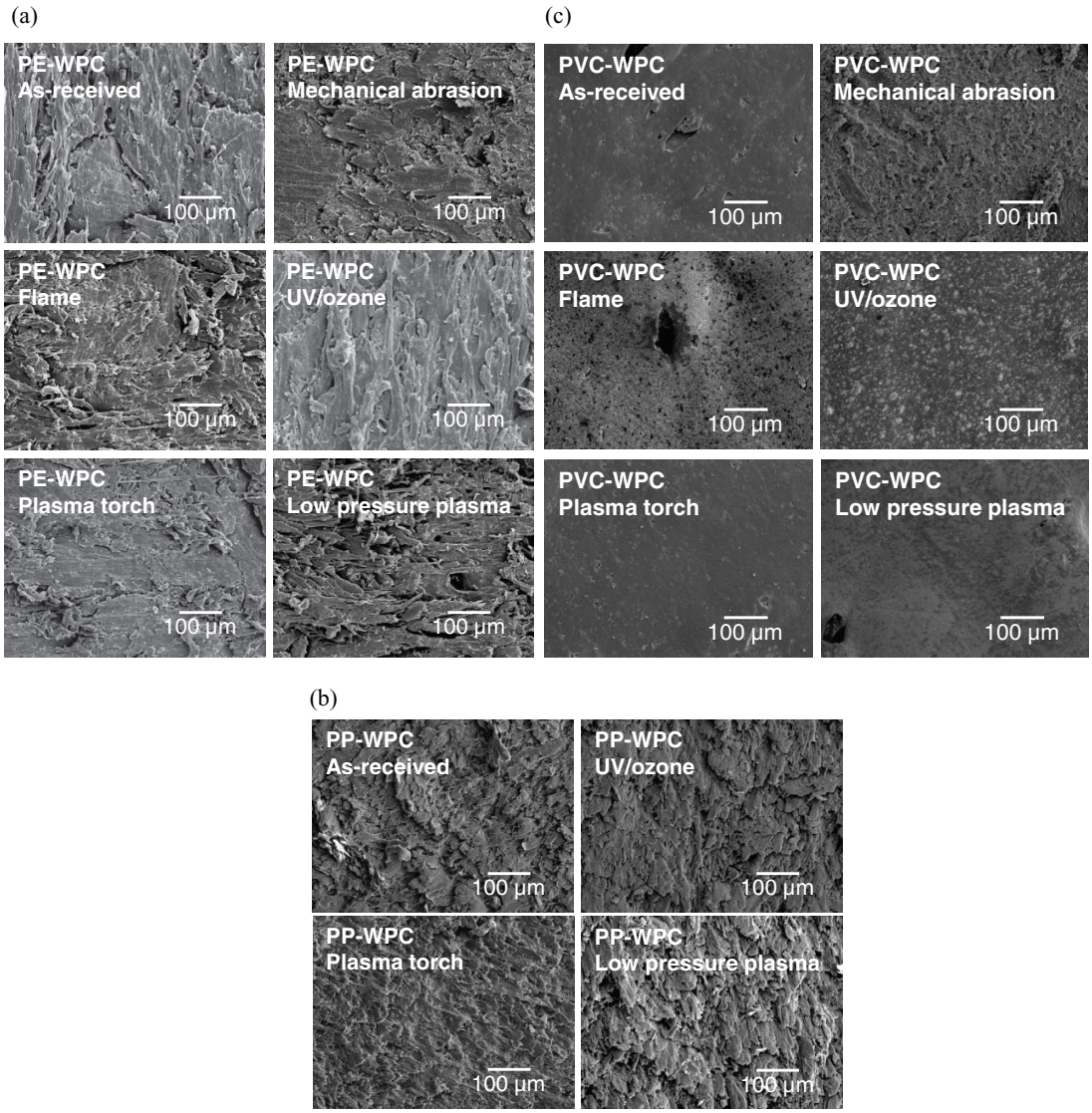

Figure 7. (a) SEM micrographs of the as-received and surface treated PE-WPC. (b) SEM micrographs of the as-received and surface treated PP-WPC. (c) SEM micrographs of the as-received and surface treated PVC-WPC.

a rough surface, and all surface treatments reduce the surface roughness. The mechanical abrasion and the flame treatments produce ablation of PE-WPC mainly and low surface oxidation, this justifies the moderate increase in the surface energy. The surface of PE-WPC treated with UV/ozone, atmospheric pressure plasma torch and low pressure plasma show important ablation, the creation of pores and the surface enrichment in polyethylene; these topographical modifications together with the surface oxidation evidenced by ATR-IR spectroscopy, justify the increase in the surface energy.

The SEM micrographs of the as-received and surface treated PP-WPC are given in figure 7(b). The rough surface of the as-received PP-WPC is reduced by all surface treatments, mainly with atmospheric pressure plasma torch. The PP-WPC surfaces treated with UV/ozone and low pressure are more enriched in wood component than the one treated with atmospheric pressure plasma torch, in agreement with the evidences shown by ATR-IR spectroscopy. The highest surface energy of the low pressure plasma treated PP-WPC is due to the combination of surface oxidation and ablation.

The SEM micrographs of the as-received and surface treated PVC-WPC are given in figure 7(c). The surface of the as-received PVC-WPC is smooth, and the mechanical abrasion and flame treatments create new roughness by ablation of the outermost surface layer. The roughness of the PVC-WPC surface is not substantially modified by treatment with both plasmas, the increase in the surface energy of the plasma treated PVC-WPC can be ascribed to surface oxidation mainly. The UV/ozone treated PVC-WPC surface shows some pores and ablation which, together with the wood enriched surface and the surface oxidation, justify its high surface energy.

3.3. Adhesion properties of the WPCs

The changes in the surface chemistry, surface energy and topography of the WPCs produced by the different surface treatments should affect their adhesion.

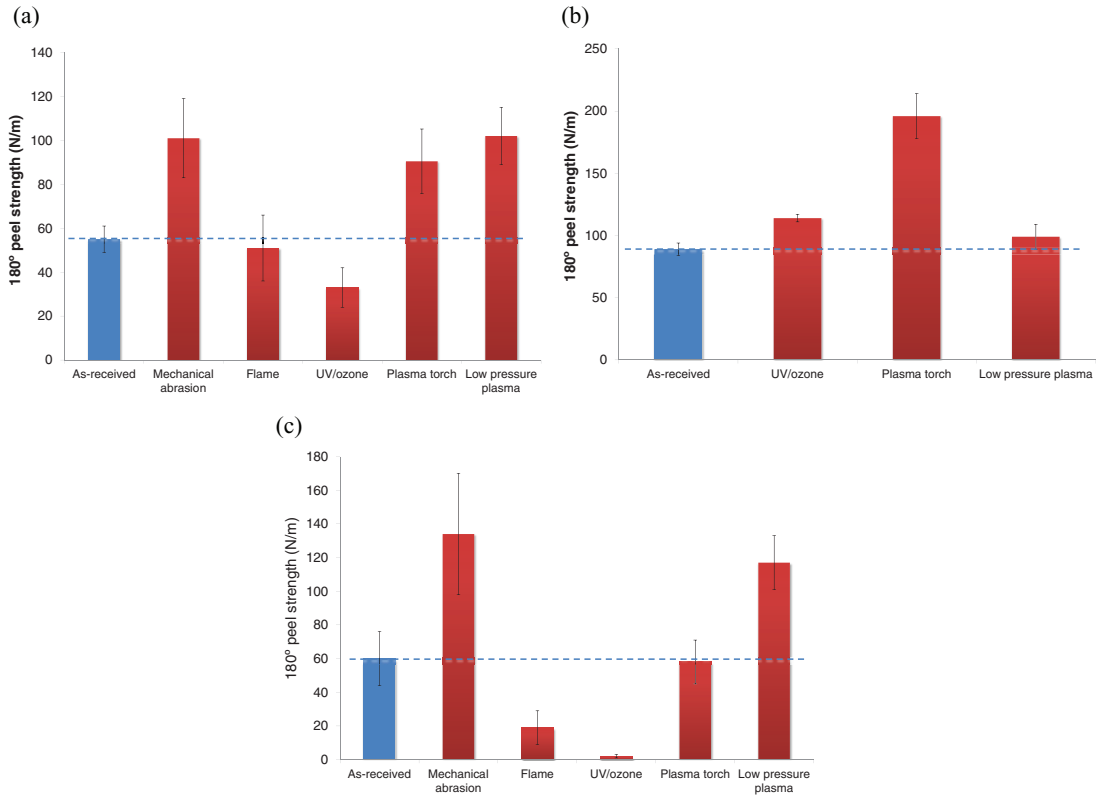

Figure 8. (a) Variation of 180° peel adhesive strength of as-received and surface treated PE-WPC/acrylic adhesive tape joints. Adhesion failure was always obtained. (b) Variation of 180° peel adhesive strength of as-received and surface treated PP-WPC/acrylic adhesive tape joints. Adhesion failure was always obtained. (c) Variation of 180° peel adhesive strength of as-received and surface treated PVC-WPC/acrylic adhesive tape joints. Adhesion failure was always obtained.

The adhesion of the as-received and surface treated WPCs was evaluated by 180° peel tests of WPC/acrylic adhesive tape joints. Acrylic adhesive tape was chosen for measuring the 'intrinsic' adhesion produced by the different treatments because it does not contain solvents and it does not show chemical cure. Therefore, high adhesion of the WPC/acrylic adhesive tape joints cannot be expected but the influence of the modifications produced in the WPC surfaces by the different surface treatments should be shown.

Figure 8(a) shows the 180° peel strength values of the as-received and surface treated PE-WPC/acrylic adhesive tape joints. The 180° peel strength of the joints made with flame and UV/ozone surface treated PE-WPC is even lower (33–52 N m^{-1}) than the one of the joint made with the as-received composite (56 N m^{-1}). Considering the surface modifications and the increase in the surface energy of PE-WPC produced by these treatments, a low adhesive strength is unexpected; one plausible explanation is the decrease in the roughness of the treated PE-WPC surface that would decrease the extent of mechanical interlocking with the acrylic adhesive. On the other hand, the 180° peel strength values of the joints made with PE-WPC treated with both plasma treatments and by mechanical abrasion are similar and higher (near to 100 N m^{-1}) than the one of the joint made with the as-received composite. The increased adhesion can be ascribed to the increase in surface energy and polarity, and the surface oxidation produced by both plasma treatments.

Figure 8(b) shows the 180° peel strength values of the as-received and surface treated PP-WPC/acrylic adhesive tape joints. All surface treatments increase the 180° peel strength. The 180° peel strength of the joints made with the as-received PP-WPC is 89 N m^{-1} and a moderate increase to 99–114 N m^{-1} is produced in the joints made with UV/ozone and low pressure plasma treated PP-WPC. However, the increase in 180° peel strength in the joints made with atmospheric pressure plasma torch treated PP-WPC is more noticeable (196 N m^{-1}), because of the surface modification, surface energy and changes in topography produced by the treatment. The 180° peel strength value obtained in the joints made with low pressure plasma are lower than expected according to the surface modifications produced by these treatments, likely due to less enriched in polypropylene surface than for the atmospheric pressure plasma torch treated PP-WPC.

Figure 8(c) shows the 180° peel strength values of the as-received and surface treated PVC-WPC/acrylic adhesive tape joints. The surface treatment of PVC-WPC with low pressure plasma and mechanical abrasion are the only ones that increase the 180° peel strength (117–134 N m^{-1}) with respect to the one of the as-received PVC-WPC (60 N m^{-1}). The treatment by mechanical abrasion improves the adhesion

Table 5. Cross-hatch adhesion values of PVA and PU coated WPCs (ASTM D3359).

		Cross-hatch adhesion—ASTM D3359		
Surface treatment	Coating	PE-WPC	PP-WPC	PVC-WPC
As-received	PU	2B (20%)	3B (10%)	0B (95%)
	PVA	4B (<5%)	4B (<5%)	0B (85%)
Mechanical abrasion	PU	—	—	—
	PVA	5B (0%)	—	—
Flame	PU	—	—	—
	PVA	5B (0%)	—	1B (50%)
UV/ozone	PU	5B (0%)	5B (0%)	4B (<5%)
	PVA	5B (0%)	5B (0%)	4B (<5%)
Atmospheric pressure plasma torch	PU	4B (<5%)	5B (0%)	5B (0%)
	PVA	5B (0%)	5B (0%)	2B (30%)
Low pressure plasma	PU	5B (0%)	5B (0%)	4B (<5%)
	PVA	5B (0%)	5B (0%)	0B (95%)

of PVC-WPC because of the creation of new surface roughness and the removal of carbonate filler and polymer from the surface. The treatment with low pressure plasma increases the adhesion of PVC-WPC due to the increase in surface energy and polarity. All other surface treatments are not sufficiently effective. According to the surface modifications produced on the atmospheric pressure plasma treated PVC-WPC, higher adhesion would be expected; however, the low adhesion can be ascribed to poor mechanical interlocking of the acrylic tape and the too smooth surface treated PVC-WPC.

In summary, the surface treatment that produces the optimal increase of 180° peel strength of the WPC/acrylic adhesive tape joint depends on the polymer nature and the wood content in the composite. The treatments by mechanical abrasion and low pressure plasma always increase the 180° peel strength, but the highest 180° peel strength values are obtained in the joints made with atmospheric pressure plasma torch treated PE-WPC and PP-WPC—the composites made with polyolefin and having higher wood content -, and with low pressure plasma or mechanical abrasion treated PVC-WPC—the composite with lower amount of wood.

The adhesion of the as-received and surface-treated WPCs was also tested by using two different liquid coatings that chemically cure during joint formation. The use of liquid coating precursors will improve the wettability of the WPC surface, and the chemical cure of the coating will favor adhesion. In order to determine the influence of the surface modifications, two liquid coating precursors—solvent-born polyurethane (PU) and waterborne polyvinyl acetate (PVA)—were applied on the as-received and treated WPC surfaces, and the cross-hatch adhesion of the coatings were measured.

Table 5 shows the cross-hatch adhesion of the coatings on WPCs measured according to ASTM 3359 standard. The cross-hatch adhesion of the as-received WPCs depends on their polymer nature and their wood content. Thus, the cross-hatch adhesion of the coated as-received PVC-WPC is very low (0B), irrespective of the coating nature, whereas the ones for PE-WPC and PP-WPC are higher (2B-4B), particularly for the PVA coated as-received WPCs (table 5, figures 9(a) and (b)). The lower cross-hatch adhesion of the coated as-received PVC-WPC can be ascribed to the absence of surface roughness and its high polymer content. Irrespective of the coating nature and the surface treatment, the cross-hatch adhesion of the coated PE-WPC and PP-WPC is notably improved (4B-5B), i.e. the maximum cross-hatch adhesion is obtained in the most of the coatings. The improved cross-hatch adhesion of the coated surface treated PE-WPC and PP-WPC can be attributed to the improved surface energy and surface ablation produced by the different surface treatments. On the other hand, all surface treatments improve the adhesion of PVC-WPC to all coatings, particularly for the polyurethane coating, the PVA coated low pressure plasma treated PVC-WPC is an exception. The UV/ozone treatment produces the highest cross-hatch adhesion (4B) of the coated PVC-WPC, irrespective of the coating nature, and the plasma treatments are quite efficient in increasing the cross-hatch adhesion of PU coated plasma treated PVC-WPC. The cross-hatch adhesion of the PVA coated surface treated PVC-WPC is lower than for the PU coated one, likely due to the different chemical nature and the different solvents of the coatings. Interestingly, the trends in 180° peel strength and cross-hatch adhesion values are very different for the surface treated PVC-WPC likely due to its lower wood content and absence of roughness and porosity.

In summary, the application of liquid chemically cure coatings enhances the adhesion of the WPCs, the effectiveness of the surface treatment is depending on their wood content and polymer nature. However, the surface treatment with atmospheric pressure plasma torch and UV/ozone always produced important improvement in adhesion in all WPCs irrespective of the coating nature. Figures 9(a) and (b) shows

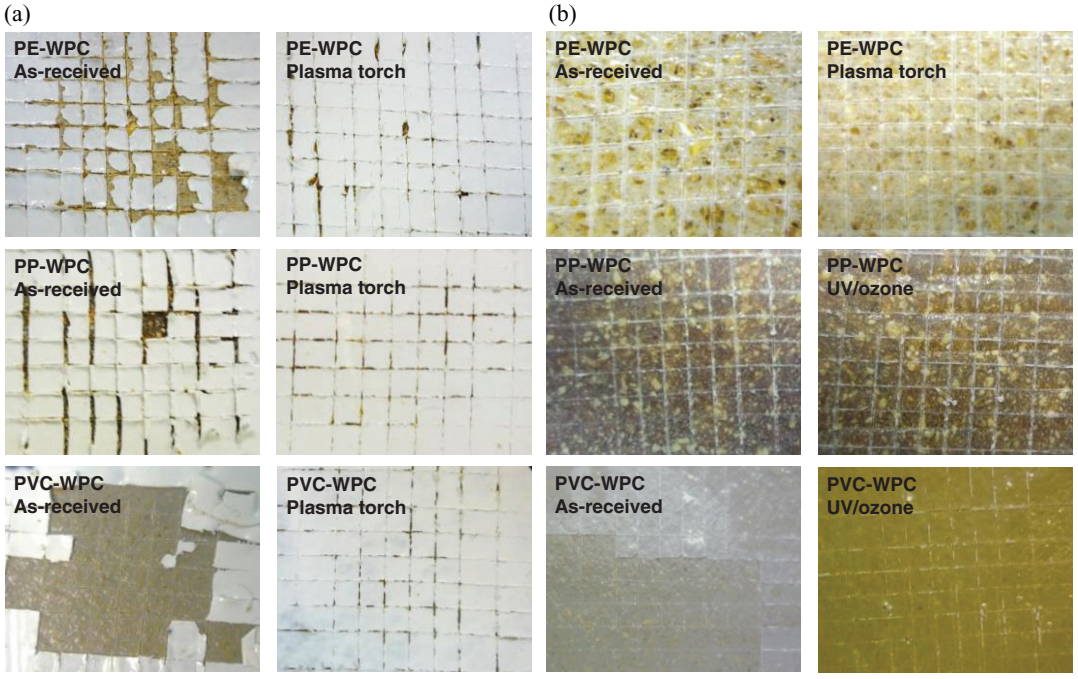

Figure 9. (a) Photos of the PU coated as-received and atmospheric pressure plasma torch treated WPCs, after cross-hatch adhesion test. (b) Photos of the PVA coated as-received and surface treated WPCs, after cross-hatch adhesion test.

some photos of the PU and PVA coated as-received and surface treated WPCs after cross-hatch adhesion test, respectively. These photos evidence the improvement in the cross-hatch adhesion of all surface treated WPCs.

4. Conclusions

Three WPCs made with different wood content and polymer nature have been surface treated under the optimal experimental conditions by mechanical abrasion, flame, and radiation-based (UV/ozone, atmospheric pressure plasma torch, Ar:O_2 low pressure plasma) treatments. The radiation-based treatments were the most efficient in increasing the wettability and the surface energy, mainly the polar component of the surface energy, and the extent of surface oxidation and ablation of the WPCs. Whereas the radiation-based surface treatments produced an enrichment in polymer surface and surface oxidation of PE-WPC and PP-WPC, the UV/ozone treatment was the only producing an enriched in wood surface and surface oxidation of PVC-WPC. On the other hand, the surface roughness was reduced and ablation was enhanced more in the surface treated PE-WPC and PP-WPC than in PVC-WPC.

The 180° peel strength and cross-hatch adhesion of the radiation-based surface treated PE-WPC and PP-WPC increased, irrespective of the adhesive and coating nature. The highest increase in adhesion was obtained for the joints made with atmospheric pressure plasma torch treated PE-WPC and PP-WPC. Because of the higher wettability and chemical cure of the coatings, higher cross-hatch adhesion than 180° peel strength values were obtained. The lowest adhesion was obtained in the joints made with surface treated PVC-WPC and the effectiveness of the surface treatments was lower than for PE-WPC and PP-WPC. However, the UV/ozone treatment increased notably the cross-hatch adhesion of PVC-WPC, mainly to PU coating, but the 180° peel strength was quite low. The smooth PVC-WPC surface, its low wood content and the presence of carbonate filler in its composition were responsible of the different trends in 180° peel strength and cross-hatch adhesion.

In summary, the wood content and polymer nature, and the surface roughness too, determined the effectiveness of the surface treatment of the WPCs, UV/ozone and atmospheric pressure plasma torch were the most efficient surface treatments for PE-WPC and PP-WPC. AQ2

Acknowledgments

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References

AQ5

[1] Klyosov A A 2007 *Wood-Plastic Composites* (New Jersey: Wiley)
[2] Niska K O and Sain M (ed) 2008 *Wood-Polymer Composites* (Woodhead Publishing)

AQ6

[3] Kraus E, Baudrit B, Heidemeyer P, Bastian M, Stoyanov O V and Starostina I A 2015 Problems in adhesion bonding of WPC *Polym. Res. J.* **9** 327–35
[4] Ryntz R A 1998 *Adhesion to Plastics—Molding and Paintability* 1st edn (Chicago, IL: Global Press) p 112
[5] Gramlich W M, Gardner D J and Neivandt D J 2006 *J. Adhes. Sci. Technol.* **20** 1873–87
[6] Dimitriou A, Hale M D and Spear M J 2016 *Int. J. Adhes. Adhes.* **68** 816–94
[7] Oporto G S, Gardner D J, Bernhardt G and Neivandt D J 2007 *J. Adhes. Sci. Technol.* **21** 1097–16
[8] Moghadamzadeh H, Rahimi H, Asadollahzadeh M and Hemmati A R 2011 *Int. J. Adhes. Adhes.* **31** 816–21
[9] Gupta B S and Laborie M-P G 2007 *J. Adhes.* **83** 939–55
[10] Yáñez-Pacios A J and Martín-Martínez J M 2018 *Plasma Chem. Plasma Process.* accepted
[11] Hünnekens B, Krause A, Militz H and Viöl W 2017 *Eur. J. Wood Prod.* **75** 761–6
[12] Yáñez-Pacios A J and Martín-Martínez J M 2017 *Int. J. Adhes. Adhes.* **77** 204–13
[13] Hämäläinen K and Kärki T 2013 *Adv. Mat. Res.* **718–20** 176–85
[14] Liu Y, Tao Y, Lv X, Zhang Y and Di M 2010 *Appl. Surf. Sci.* **257** 1112–8
[15] Hünnekens B, Peters F, Avramidis G, Krause A, Militz H and Viöl W 2016 *J. App. Polym. Sci.* **133** 43376
[16] Wolkenhauer A, Avramidis G, Hauswald E, Militz H and Viöl W 2008 *J. Adhes. Sci. Technol.* **22** 2025–37
[17] Yáñez-Pacios A J and Martín-Martínez J M 2017 *Compos. Interfaces* **25** 127–49
[18] Stark N M, Matuana L M and Clemons C M 2004 *J. Appl. Polym. Sci.* **93** 1021–30

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